ARSENIC AND OTHER NATURALLY-OCCURRING ELEMENTS

ARSENIC - WHAT IS IT?

Arsenic is an odorless and tasteless, naturally occurring element present in soil and rock. Under certain environmental conditions, arsenic can dissolve and be transported in groundwater. It can also be released as a by-product from agricultural and industrial activities. Everyone is exposed to small amounts of arsenic since it is a natural part of the environment, but under some geologic conditions elevated amounts of arsenic can be released to groundwater.

The Wisconsin State health-based groundwater quality enforcement standard (ES) for arsenic in groundwater, and the maximum contaminant level (MCL) for arsenic in public drinking water, are both 10 parts per billion (ppb), or 10 micrograms per liter (ug/L) (WI NR 140.10, WI NR 809.11). People who drink water containing arsenic in excess of the 10 ppb MCL over many years could experience skin damage or problems with their circulatory system, nervous system, and have an increased risk of getting cancer.

Occurrence in Wisconsin

In Wisconsin, most arsenic found in groundwater is naturally occurring, released from minerals in bedrock and glacial deposits. Arsenic has been detected above the ES in the groundwater in every county in Wisconsin. Arsenic contamination of groundwater is common in northeastern Wisconsin in areas around Winnebago and Outagamie County and moderately high levels of arsenic (10 ppb – 30 ppb) are also common in some parts of southeastern Wisconsin.

Arsenic is common in northeastern Wisconsin (regions 1 and 3) and southeastern Wisconsin. *Figure*: *Luczaj and Masarik, 2015*.

In *northeastern Wisconsin*, a geologic formation called the St. Peter Sandstone contains arsenic-rich minerals. When sulfide minerals common in this rock are exposed to oxygen in the air – either at the water table elevation or from drilling activity – chemical reactions solubilize these minerals and lead to very high levels of arsenic in water (exceeding 100 ppb, or 10 times the ES). In low-oxygen groundwater environments, arsenic can be released from the St. Peter Sandstone at lower concentrations which may still exceed the ES. This more moderate contamination may result from the same sulfide minerals or from arsenic that is bound to iron oxide minerals.

In *southeastern Wisconsin*, most wells draw from glacial sand and gravel deposits or from Silurian dolomite bedrock formations. While oxidizing conditions tend to release arsenic from sulfide minerals in northeastern Wisconsin, reducing conditions (where dissolved oxygen is low) tend to release arsenic from iron compounds in the glacial deposits and dolomite of southeastern Wisconsin.

In *northern* Wisconsin sulfides and arsenopyrite can be found in the Precambrian granitic bedrock, and arsenic bearing iron oxides can be in the end moraine deposits of various glacial advances.

In *southwestern* Wisconsin sulfides associated with the lead-zinc district have contaminated a number of wells. Further north, sulfides in the Tunnel City formation have forced the replacement of at least a dozen wells from La Crosse to Barron counties. A report by Zambito, et. al. (2019) explains the occurrence of arsenic and metal bearing sulfides. Other metals commonly associated with arsenic are nickel, cobalt, copper, aluminum and vanadium.

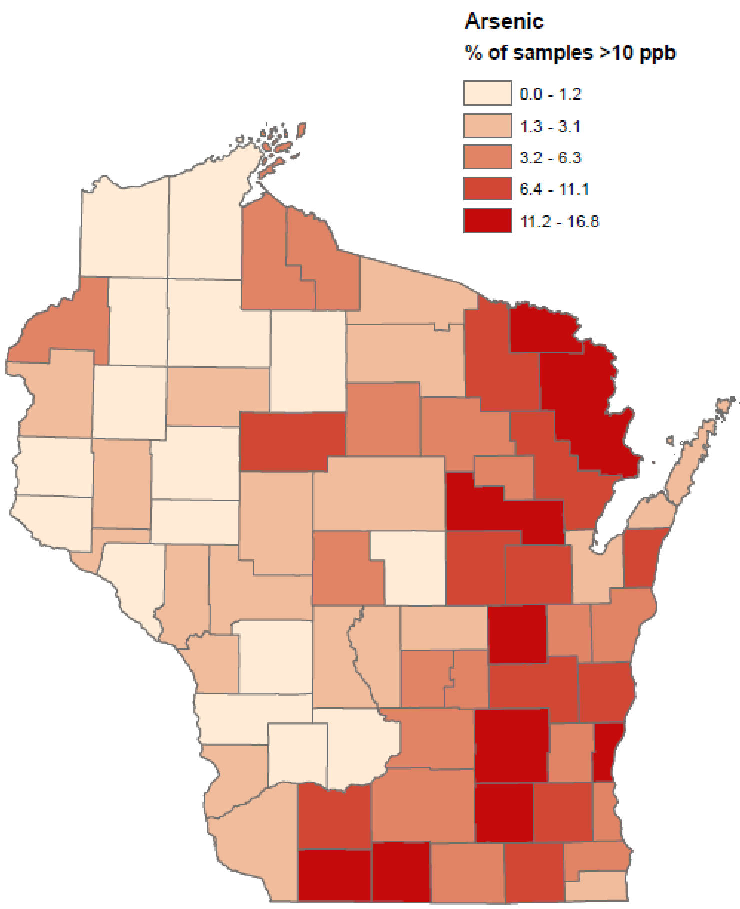
GCC Agency Actions

Naturally-occurring arsenic was unexpectedly discovered in Wisconsin in 1987 during a feasibility study for a proposed landfill in Winnebago County. Follow up sampling by DNR and reports from nearby homeowners revealed a pressing need to determine the distribution and frequency of the problem. As a result, over the next several years DNR, the Department of Health Services (DHS) and local health officials teamed with researchers funded by the Wisconsin Groundwater Research and Monitoring Program (WGRMP) to sample thousands of private wells in the Winnebago and Outagamie County area and analyze where and why arsenic levels were elevated (Burkel, 1993; Burkel and Stoll, 1995). As researchers identified first the geologic formation, then the chemical reactions responsible for the situation (Pelczar, 1996; Simo, 1995 and 1997; Gotkowitz et al., 2003), the DNR outlined a Special Well Casing Depth Area and developed well construction guidelines to protect drinking water wells in this area from contamination. Simultaneously, DHS worked with local health officials to inform residents of health risks, provided low-cost testing of private wells, and gathered information about people with long-term exposure to arsenic in one of the largest epidemiological studies ever conducted in Wisconsin (Knobeloch et al, 2002; Zierold et al., 2004).

In the early 2000s, the US EPA lowered the MCL for arsenic from 50 ppb to 10 ppb (the current standard), which raised concerns for schools and residents in southeastern Wisconsin that had been observing arsenic levels in the 10-50 ppb range. Initial testing by the DNR and the Wisconsin Geological and Natural History Survey (WGNHS) revealed that the geochemical explanations for arsenic contamination in northeastern Wisconsin could not explain the problem in southeastern Wisconsin (Gotkowitz, 2002), so the WGRMP funded further research to analyze the new situation and develop more appropriate guidelines (Sonzogni et al., 2003; Bahr et al., 2004; Root 2005; West et al., 2012). One of the important outcomes of these studies was improved understanding of how chlorine disinfection, which is often used to treat microbial biofilms (slime) in wells, can affect the release of arsenic (Gotkowitz et al, 2008). Shock chlorination of private wells should be limited in much of northeastern Wisconsin because it has a strongly oxidizing effect that encourages release of arsenic from sulfide minerals. Well chlorination does not similarly affect arsenic bound to iron compounds in groundwater environments such as southeastern Wisconsin. In these settings, well disinfection may in fact reduce arsenic levels by controlling microbes that contribute to iron dissolution.

The extensive research completed in Wisconsin over the past 20 years illustrates the highly variable nature of Wisconsin's geologic sources of arsenic to groundwater. A well with no detectable arsenic can be right across the street from a well that tests well above the 10 ppb MCL. Arsenic concentrations can vary over time, too. This makes regular testing – with efficient, accurate and affordable methods - critical. WGRMP-funded researchers have been important partners in this effort and have designed portable field sampling kits, improved upon existing laboratory methods and are currently working on sensors that can immediately detect arsenic levels in groundwater. Most recently a project has begun looking at the association of bedrock fold and faults with arsenic contamination.

In 2014, the DNR began requiring testing for arsenic when pump work was being done on existing wells. The data is being analyzed to determine if additional Special Well Casing Depth Areas should be developed.



Map 1. Beginning in 2014 the department has required arsenic sampling when pump work is done on existing wells. The map above is from the 35,000+ samples collected over the first 7 and a half years. The map depicts the percent of wells over 10 ppb arsenic in each county (see tabular data below). This analysis shows that arsenic is more widespread than previously thought.

County	% >10		County	% >10
Adams	1.3		Marathon	2.1
Ashland	3.4		Marinette	16.8
Barron	1.0		Marquette	4.2
Bayfield	0.6		Menominee	4.9
Brown	2.0		Milwaukee	4.3
Buffalo	0.6		Monroe	0.6
Burnett	3.5		Oconto	10.5
Calumet	3.5		Oneida	1.5
Chippewa	0.6		Outagamie	10.6
Clark	2.4		Ozaukee	16.6
Columbia	5.8		Pepin	2.8
Crawford	1.6		Pierce	0.2
Dane	4.7		Polk	2.2
Dodge	13.4		Portage	0.9
Door	1.8		Price	1.0
Douglas	0.5		Racine	5.7
Dunn	1.9		Richland	0.2
Eau Claire	1.0		Rock	3.2
Florence	14.7		Rusk	1.5
Fond du Lac	9.4		Saint Croix	0.8
Forest	6.6		Sauk	0.9
Grant	1.9		Sawyer	0.9
Green	11.1		Shawano	15.8
Green Lake	5.7		Sheboygan	10.0
Iowa	7.6		Taylor	10.2
Iron	3.7		Trempealeau	2.5
Jackson	2.0		Vernon	0.0
Jefferson	12.0		Vilas	1.7
Juneau	1.7		Walworth	6.7
Kenosha	3.1		Washburn	0.9
Kewaunee	7.0		Washington	5.9
La Crosse	2.8		Waukesha	7.5
Lafayette	15.5		Waupaca	6.5
Langlade	5.3		Waushara	2.1
Lincoln	3.3		Winnebago	15.9
Manitowoc	3.6		Wood	3.9

Table 1. Percent of wells over 10 ppb arsenic by county.

Arsenic continues to be an issue for Wisconsin well owners. In 2021 the pump work samples for 374 wells were over the Enforcement Standard (ES) at 5%, and 2,042 were over the Preventive Action Limit (PAL) at 28%, with a maximum level of 1,290 ppb. In addition department staff reviewed and responded to over 70 sample results from the Wisconsin State Lab of Hygiene that were over 10 ppb.

Future Work

Sampling and testing private wells remain important priorities for understanding and managing arsenic contamination in Wisconsin. To encourage private well sampling, local health departments continue to offer fee-exempt testing to low income families. The DNR and some county governments are also working to both promote well sampling programs and explore impediments to private well sampling.

Arsenic-rich minerals, such as arsenic-rich pyrite (pictured), are natural sources of arsenic in groundwater in Wisconsin. *Photo: JJ Harrison.*

In areas of the state known to be vulnerable to arsenic contamination, there is a focus on reducing exposure. Several communities have expanded the service area for public water systems and moved homes from private wells to public supplies. This expansion has been effective in reducing exposure in towns like Algoma in Winnebago County.

Areas outside the original region of concern in northeast Wisconsin and the more recent area of concern in southeast Wisconsin have not been as well described. Revisions to NR 812 now require wells to be tested for arsenic, in addition to bacteria and nitrate, during pump installation or when testing is requested during property transfers involving existing private wells. This may help to fill the data gap. In addition, researchers from the WGNHS funded by the WGRMP are currently working to understand the mineralogy of the Tunnel City rock formation in western Wisconsin, which may help define the risk of arsenic contamination in that region.

Discovery triggers geochemical questions, science improves understanding and helps GCC agencies better protect human health – this pattern is repeated by GCC agencies and researchers whenever natural contaminants are identified in groundwater in unexpected amounts in a new location. This continues today with ongoing investigations that are exploring the occurrence of strontium near Green Bay and the presence of heavy metals in geologic formations near La Crosse, among others.

OTHER NATURAL CONTAMINANTS IN WI GROUNDWATER

NATURALLY-OCCURRING RADIONUCLIDES

Radionuclides are radioactive atoms. It is possible for radionuclides to be manmade, as is the case with some materials from nuclear power reactors, but they also occur naturally in rock formations and are released to groundwater over millions of years by geochemical reactions. Common naturally-occurring radionuclides in groundwater include uranium and thorium, which both decay to different forms of radium, which in turn decays to radon. General indicators of high-energy radiation are monitored in water as alpha, beta, and gamma (now included in a broader group called photon emitters) activity.

There are no ch. NR 140 groundwater quality standards for radionuclides in Wisconsin but MCLs for public drinking water systems have been established for the radionuclides uranium and (total) radium, and for alpha and beta (plus photon) particle activity. No public water supply MCL has been established for radon but the United States Environmental Protection Agency (US EPA) has proposed that radon levels in water be no higher than 4,000 picocuries per liter (pCi/L), where indoor air radon abatement programs exist, and no higher than 300 pCi/L where indoor air radon abatement programs do not exist.

RADIUM IN SOUTHEASTERN WISCONSIN

A well-known example of natural contamination in Wisconsin is radium in southeastern Wisconsin. By the late 1990s, drawdown in this region due to decades of large-scale pumping was causing concerning increases in radium levels in drinking water. Initial links between radium and geologic formations in eastern Wisconsin had been drawn by GCC researchers in 1990 (Taylor and Mursky, 1990), but the source of radium was poorly understood, making it difficult to know how to manage drinking water sources. Research funded by the WGRMP in the late 1990s more clearly demonstrated that high radium is most common near the edge of the Maquoketa shale, which runs from Brown County in the north to Racine County in the south (Grundl, 2000).

A remaining puzzle was why radium levels were elevated to the east of the Maquoketa shale boundary but not to the west – conventional understanding of the sources of radium did not seem sufficient to explain observations. In the early 2000s, researchers at the University of Wisconsin and the Wisconsin Geological and Natural History Survey (WGNHS) leveraged new models and knowledge about groundwater flow patterns in the Waukesha area to elucidate the relationship between radium and sulfate minerals in the area, collecting much needed information on the geochemical backdrop of the region in the process (Grundl et al., 2003). Today, there are still unanswered questions about the precise geochemical processes that control radium activity, but our improved understanding of radium sources helps water managers in eastern Wisconsin define their options: treat water from deep aquifers, blend with water from shallow aquifers, or find alternate surface sources for drinking water.

NATURALLY-OCCURRING CHROMIUM IN GROUNDWATER

As water flows underground, metals such as chromium, may be dissolved from rock or soil and be mobilized, and therefore present in groundwater. Natural sources of chromium in groundwater include some types of igneous bedrock and soils derived from those bedrock sources. In groundwater, chromium can generally be found in one of two forms, as trivalent chromium (Cr lll), or chromium-3, or as hexavalent chromium (Cr VI), or chromium-6. While trivalent chromium is an essential nutrient, hexavalent chromium is acutely toxic and has been classified as "likely to be carcinogenic to humans". Water quality analysis for chromium is generally done for "total chromium" (trivalent chromium + hexavalent chromium). The US EPA has established a public water supply MCL for total chromium at 100 micrograms per liter (μg/L) and, in Wisconsin, the ch. NR 140 groundwater quality enforcement standard (ES) for total chromium is 100 μg/L. The DHS has recently recommended a ch. NR 140 ES for hexavalent chromium of 70 nanograms per liter (ng/L).

CHROMIUM IN DANE COUNTY

In Dane County, residents were surprised to learn in 2011 that hexavalent chromium (Cr [VI]) is present in Madison drinking water in very low concentrations. While trivalent chromium (Cr [III]) is an essential trace nutrient in low concentrations, Cr (VI) is a suspected carcinogen. As DHS responded to questions about the health effects of Cr (VI), WGNHS quickly embarked on a sampling study to determine whether there was a naturally occurring source of chromium in the local bedrock formations (Gotkowitz et al., 2012). Findings indicate that chromium naturally occurs in all formations, but only the upper aquifers seem to have the geochemical conditions to promote mobility of aqueous Cr (VI).

Sampling irrigation wells for Cr (VI). *Photo: Patrick Gorski*

WGRMP-funded researchers at UW-Madison and the Wisconsin State Laboratory of Hygiene followed up with a project to explore what geochemical environments create ideal conditions for Cr (VI) mobility in key geologic formations across the state (Gorski et al., 2015). Work like this helps Wisconsin communities prepare for a federal drinking water standard for Cr (VI), which does not currently exist but is expected to in the future.

NATURALLY-OCCURRING STRONTIUM IN GROUNDWATER

Naturally occurring, non-radioactive strontium is present in Wisconsin groundwater and has been found at very high concentrations in some parts of the State. Non-radioactive, or "stable strontium", naturally occurs in rock and soil and, under certain geochemical conditions, is dissolved from rock and soil sources and mobilized in groundwater. Very high levels of naturally occurring strontium have been documented in municipal water supply wells in eastern Wisconsin (USGS 1963). Strontium's chemical behavior is similar to calcium and strontium minerals have been found in carbonate bedrock deposits in Wisconsin. The weathering and dissolution of carbonate bedrock containing strontium minerals may be a source of elevated strontium in groundwater. Highly mineralized brines have also been shown to contain very high levels of dissolved strontium. No public water supply MCL has been established for strontium, but the US EPA has established a lifetime health advisory level for strontium in drinking water at 4,000 µg/L. The DHS has recently recommended a ch. NR 140 ES for strontium of 1,500 µg/L.

A research project, funded through WGRMP, was conducted to study the occurrence and sources of strontium in groundwater in northeastern Wisconsin (Luczaj 2013). Very high levels of strontium in wells drawing water from the Cambrian Ordovician bedrock aquifer in the northeast part of the state were documented in the study. The research found that groundwater chemistry in the Cambrian Ordovician aquifer was influenced by deep regional bedrock faults, that created aquifer groundwater “zones” with differing major ion chemistry. Strontium minerals, precipitated from Michigan geologic basin hydrothermal brines, in carbonate bedrock and interstitial cement in sandstone formations were determined to be the likely source of elevated strontium in groundwater. The heterogenous nature of bedrock strontium mineral deposition, and the influence of major faults on groundwater chemistry, were suggested as reasons for the observed variability in strontium concentrations in well water across the study area.

UPDATE ON GROUNDWATER STANDARDS RELATED TO NATURALLY-OCCURRING ELEMENTS IN WI GROUNDWATER

Strontium, hexavalent chromium, aluminum, cobalt and molybdenum are all metallic elements that may be naturally occurring in rock and soil. Under certain geochemical conditions, such as reducing redox conditions, these metals may be dissolved from rock or soil and mobilized in groundwater. Anthropogenic contamination may also be the source of these metals in groundwater.

As part of a continuing commitment to protect public health, public welfare, and the environment, the DNR periodically updates groundwater quality standards in ch. NR 140, Wis. Adm. Code. In 2018 the DNR requested that DHS review toxicological information and, if warranted, provide new or updated groundwater quality standards for substances found in Wisconsin groundwater. In 2019, as part of ch. NR 140 "Cycle 10", DHS provided recommendations for new and revised groundwater quality standards for strontium, hexavalent chromium, aluminum, cobalt and molybdenum (see https://www.dhs.wisconsin.gov/water/gws-cycle10.htm). On February 23, 2022, the DNR Natural Resources Board (NRB) considered approval of proposed revisions to ch. NR 140 to incorporate the DHS NR 140 Cycle 10 groundwater standard recommendations, including the recommended new and updated standards for strontium, hexavalent chromium, aluminum, cobalt and molybdenum. The NRB did not approve the proposed NR 140 Cycle 10 groundwater quality standards.

Further Reading

DNR overview of arsenic in drinking water wells

DNR special well casing depth areas for arsenic

DHS overview of arsenic health effects

WGNHS report on arsenic release due to well disinfection

WGNHS report on preliminary investigation near Lake Geneva, Wisconsin

DHS report on arsenic in Wind Lake Private Wells, Town of Norway, Racine County

Wisconsin Natural Resource magazine article on arsenic in private wells (December 2000)

Origin and Distribution of Dissolved Strontium in the Cambrian-Ordovician Aquifer of Northeastern Wisconsin

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Hexavalent Chromium (Cr(VI)) in WI Groundwater: Identifying Factors Controlling the Natural Concentration and Geochemical Cycling in a Diverse Set of Aquifers

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